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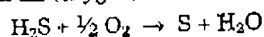
SECTION 22

Sulfur Recovery

Sulfur is present in natural gas principally as hydrogen sulfide (H_2S) and, in other fossil fuels, as sulfur-containing compounds which are converted to hydrogen sulfide during processing. The H_2S , together with some or all of any carbon dioxide (CO_2) present, is removed from the natural gas or refinery gas by means of one of the gas treating processes described in Section 21. The resulting H_2S -containing acid gas stream is flared, incinerated, or fed to a sulfur recovery unit. This section is concerned with recovery of sulfur by means of the modified Claus and Claus tail gas clean-up processes. Redox processes are touched upon. For a discussion and description of other sulfur recovery processes, see Maddox¹.

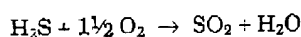
THE CLAU PROCESS

The Claus process as used today is a modification of a process first used in 1883 in which H_2S was reacted over a catalyst with air (oxygen) to form elemental sulfur and water.



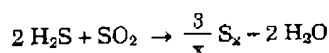
Control of this highly exothermic reaction was difficult and sulfur recovery efficiencies were low. In order to overcome these process deficiencies, a modification of the Claus process was developed and introduced in 1936 in which the overall reaction was separated into (1) a highly exothermic thermal or combustion reaction section in which most of the overall heat of reaction (from burning one-third of the H_2S and essentially 100% of any hydrocarbons and other combustibles in the feed) is released and removed, and (2) a moderately exothermic catalytic reaction section in which sulfur dioxide (SO_2) formed in the combustion section reacts with unburned H_2S to form elemental sulfur. The principal reactions taking place (neglecting those of the hydrocarbons and other combustibles) can then be written as follows:

Thermal or Combustion Reaction Section



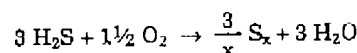
$$\Delta H @ 77^\circ\text{F} = -223\,100 \text{ Btu}$$

Combustion and Catalytic Reaction Sections



$$\Delta H @ 77^\circ\text{F} = -41\,300 \text{ Btu}$$

Overall Reaction



$$\Delta H @ 77^\circ\text{F} = -264\,400 \text{ Btu}$$

This is a simplified interpretation of the reaction actually taking place in a Claus unit. The reaction equilibrium is complicated by the existence of various species of gaseous sulfur (S_2 , S_3 , S_4 , S_6 , S_7 , and S_8) whose equilibrium concentrations in relation to each other are not precisely known for the entire range of process conditions. Furthermore, side reactions involving hydrocarbons, H_2S , and CO_2 present in the acid gas feed can result in the formation of carbonyl sulfide (COS), carbon disulfide (CS_2), carbon monoxide (CO), and hydrogen (H_2). Gamson and Elkins² cover the basic theory involved in the Claus process; however, they ignore the many potential side reactions and also the existence of S_3 , S_4 , S_5 , and S_7 .

For the usual Claus plant feed gas composition (water-saturated with 30-80 mol % H_2S , 0.5-1.5 mol % hydrocarbons, the remainder CO_2), the modified Claus process arrangement results in thermal section (burner) temperatures of about 1800 to 2500°F. The principal molecular species in this temperature range is S_2 (Fig. 22-19) and conditions appear favorable for the

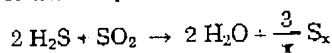
FIG. 22-1

Nomenclature

H = heat content or enthalpy, Btu/lb or Btu/lb-mole

K_p = equilibrium constant

For the low pressure, vapor phase Claus reaction



$$K_p = \frac{(P_{\text{H}_2\text{O}})^2 (P_{\text{S}_x})^{3/x}}{(P_{\text{H}_2\text{S}})^2 (P_{\text{SO}_2})}$$

$$= \frac{[\text{Mols H}_2\text{O}]^2 [\text{Mols S}_x]^{3/x} \left[\frac{\pi}{\text{Total Mols}} \right]^{3/x - 1}}{[\text{Mols H}_2\text{S}]^2 [\text{Mols SO}_2]}$$

LT/D = long ton per day. A long ton is 2240 pounds.

P = partial pressure, atmospheres

π = total pressure, atmospheres

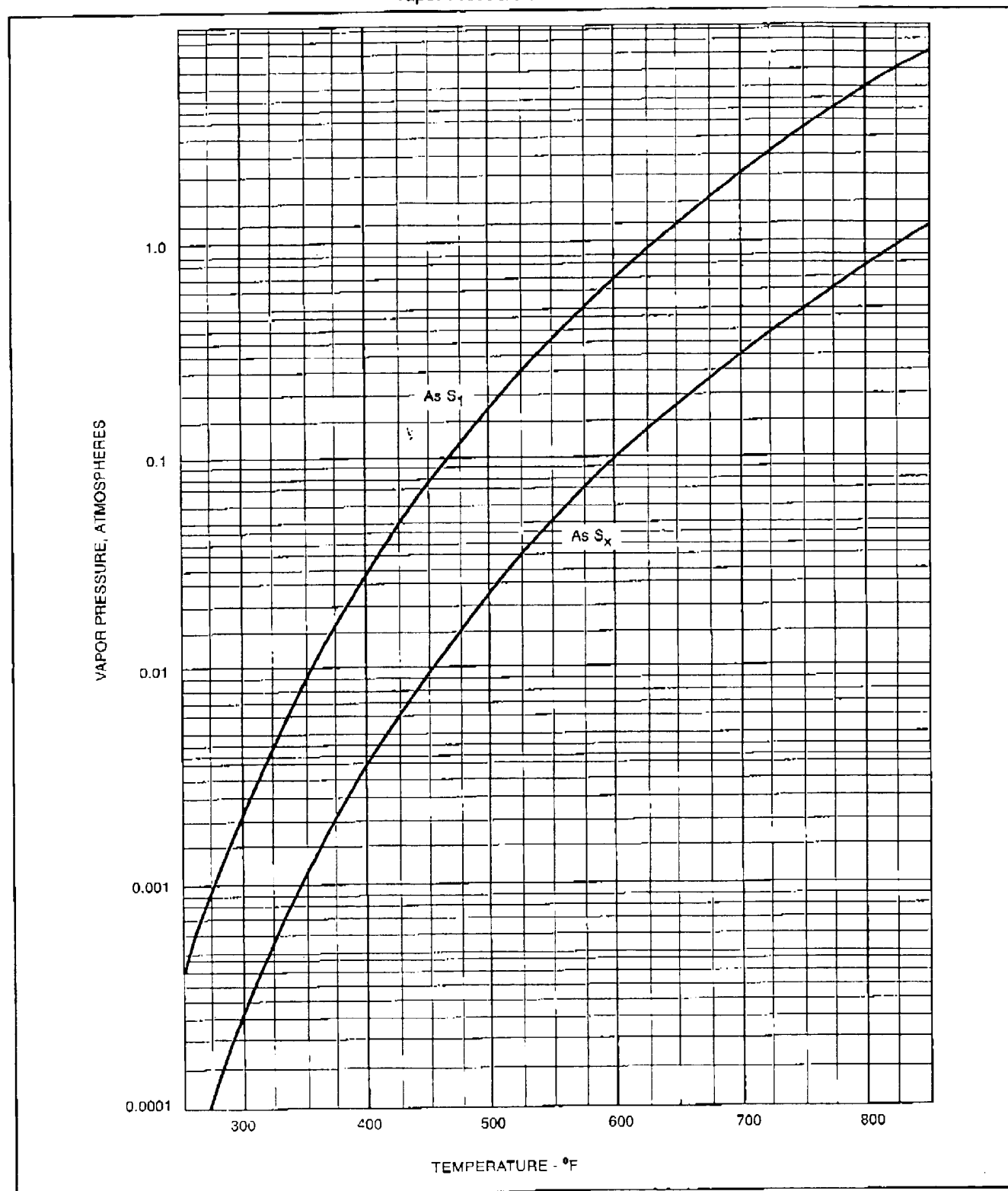
Acid Gas: feed stream to sulfur recovery plant consisting of H_2S , CO_2 , H_2O , and usually less than 2 mol % hydrocarbons.

Claus Process: a process in which $\frac{1}{3}$ of the H_2S in the acid gas feed is burned to SO_2 which is then reacted with the remaining H_2S to produce sulfur. This is also referred to as the modified Claus process.

Residence Time: the period of time in which a process stream will be contained within a certain volume or piece of equipment, seconds.

Tail Gas Cleanup Unit: a process unit designed to take tail gas from a Claus sulfur recovery plant and remove additional sulfur with the goal of meeting environmental sulfur emission standards.

FIG. 22-20
Vapor Pressure of Sulfur^{9, 20}



Appl. No. 09/625,710
Amdt. Dated August 28, 2003
Reply to Office Action of June 30, 2003
Annotated Sheet Showing Changes

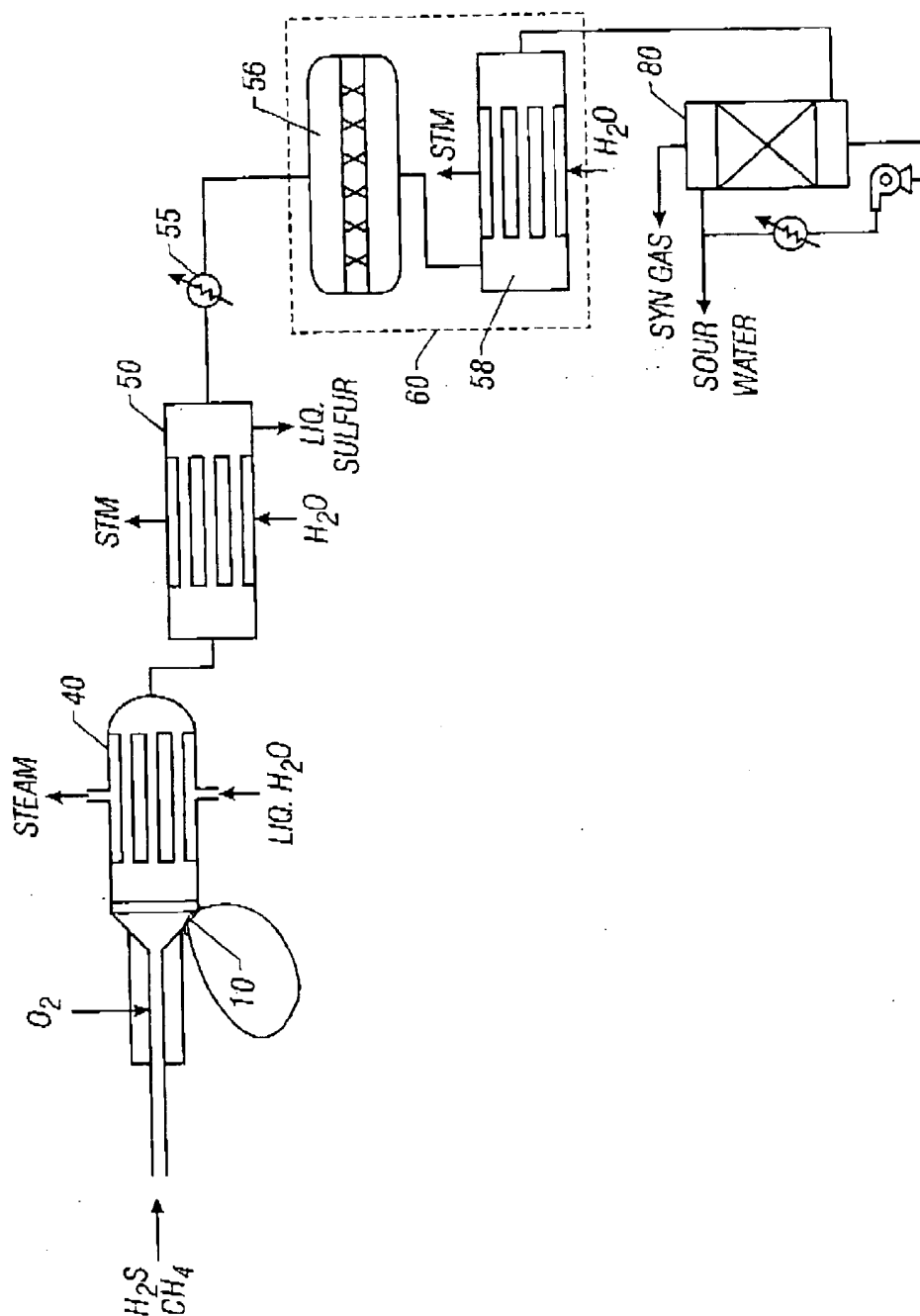


FIG. 2

Appl. No. 09/625,710
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Replacement Sheet

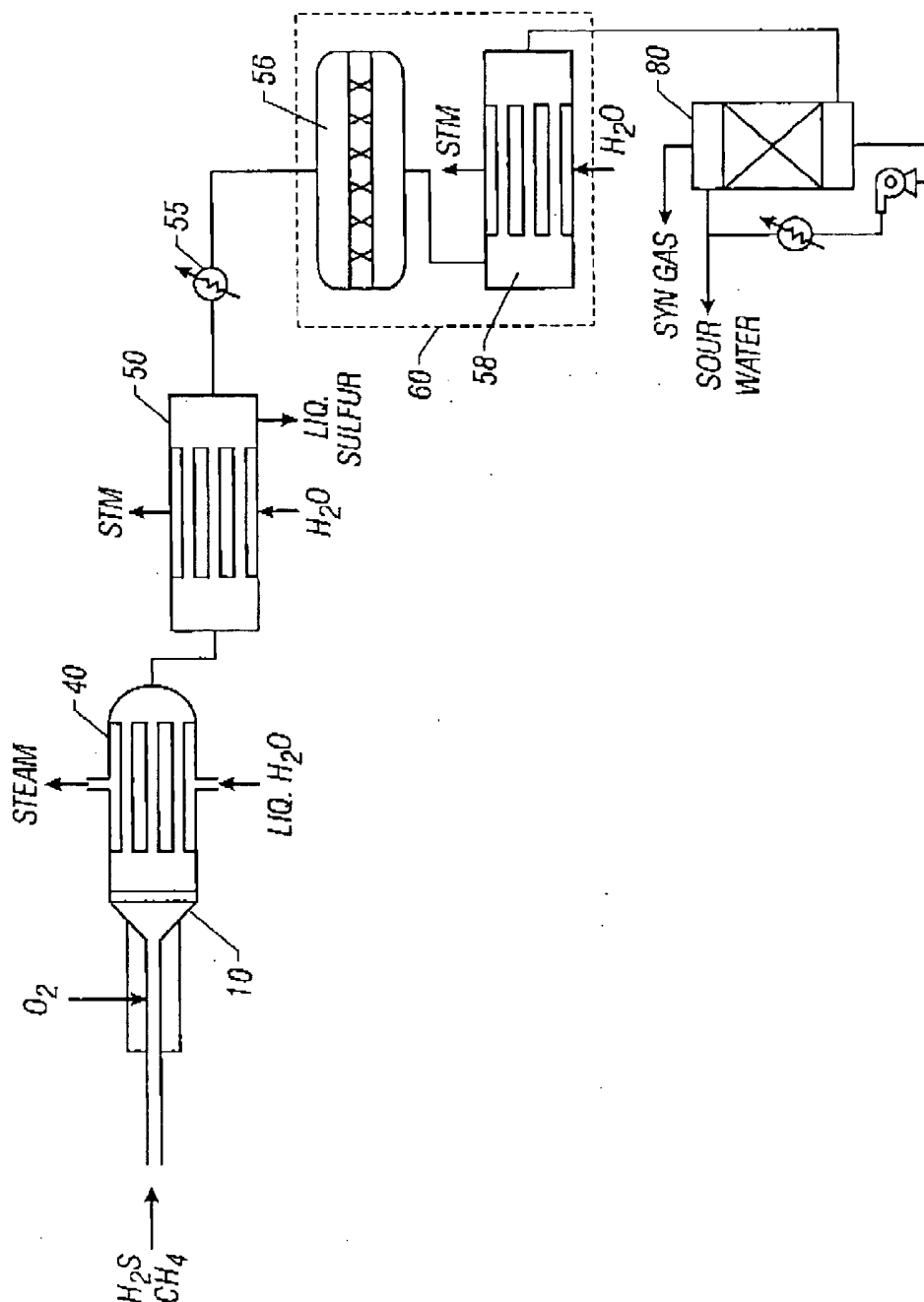


FIG. 2